PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-060716

(43)Date of publication of application : 26.02.2002

(51)Int.Cl.
C09J163/00
C08G 59/20
C09J133/08
C09J183/04
H01L 21/52
H01L 23/29
H01L 23/31

(21)Application number : 2000-253234

(22)Date of filing : 24.08.2000

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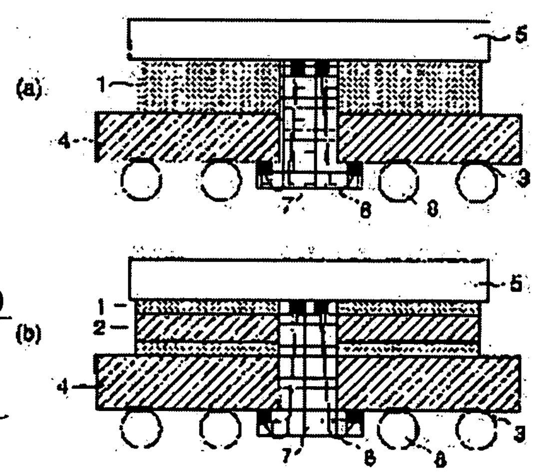
(54) LOW-ELASTIC ADHESIVE, LOW-ELASTIC ADHESIVE MEMBER, SUBSTRATE FOR LOADING SEMICONDUCTOR HAVING LOW-ELASTIC ADHESIVE MEMBER AND SEMICONDUCTOR DEVICE USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a low-elastic adhesive having heat and moisture resistances required for packaging a semiconductor chip having a great difference in coefficient of thermal expansion in a wiring substrate and capable of exhibiting good characteristics for temperature cycling tests and a low-elastic adhesive member, etc., using the low-elastic adhesive.

SOLUTION: This low-elastic adhesive comprises (1) 100 pts.wt. of the sum of an epoxy resin and a curing agent therefor, (2) 50-300 pts.wt. of an epoxy group-containing acrylic copolymer containing 2-6 wt.% of glycidyl (meth) acrylate and having ≥-10°C Tg (glass transition temperature) and ≥800,000 number-average molecular weight, (3) 0.1-10 pts.wt. of a curing accelerator, (4) 20-60 pts.wt. of a silicone rubber filler and (5) 0.1-10 pts.wt. of a coupling agent. The low-elastic adhesive member, etc., use the low-elastic adhesive.



Phenolite
elast mod
CAPLUS

DERWENT-ACC-NO: 2002-457225

DERWENT-WEEK: 200249

TITLE: Low elastic adhesive for semiconductor device, comprise specific amounts of epoxy resin, curing agent, epoxy group containing acrylic type copolymer, hardening accelerators, silicone rubber fillers and coupling agents

PATENT-ASSIGNEE: HITACHI CHEM CO LTD[HITB]

PRIORITY-DATA: 2000JP-0253234 (August 24, 2000)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP 2002060716 A	February 26, 2002	N/A	009	C09J 163/00

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP2002060716A	N/A	2000JP-0253234	August 24, 2000

INT-CL (IPC): C08G059/20, C09J133/08 , C09J163/00 , C09J183/04 , H01L021/52 , H01L023/29 , H01L023/31

ABSTRACTED-PUB-NO: JP2002060716A

BASIC-ABSTRACT:

NOVELTY - Low elastic adhesive comprises (in weight parts) epoxy resin and its curing agent (100), epoxy group containing acrylic type copolymers (EG-AC) (50-300) containing glycidyl (meth)acrylate (26 weight%), hardening accelerators (0.1-10), silicone rubber fillers (20-60) and coupling agent (0.1-10). EG-AC has glass transition temperature of -10 deg. C or more and weight average molecular weight of 800000 or more.

DETAILED DESCRIPTION - INDEPENDENT CLAIMS are also included for the following: (i) Low elastic adhesive component, which comprises low elastic adhesive layer (1) on side(s) of a base material (2); (ii) Semiconductor mounting substrate, which comprises a semiconductor chip (5) mounting surface of a wiring (3) board (4) provided with low elastic adhesive component; and (iii) Semiconductor device using the substrate for semiconductor mounting (6).

USE - For low elastic adhesive component used for mounting substrates of semiconductor devices (both claimed).

ADVANTAGE - The low elastic adhesive has excellent heat resistance, moisture resistance, adhesive property, electriecorrosion resistance during moisture absorption, wettability and bonding strength without repellence during coating. Crack generation during heat cycle test is not observed and has favorable stress-release property. Thermal stress produced due to difference in thermal expansion coefficient of semiconductor chip and wiring board, is relieved.

DESCRIPTION OF DRAWING(S) - The figures show the sectional drawings of (a) semiconductor device using adhesive component comprising monolayer of elastic adhesive and (b) semiconductor device using low elastic adhesive component equipped with base material having low elastic adhesive layer on both sides.

Low elastic adhesive layer 1

Base material 2

Wiring 3

AN 2002:147802 CAPLUS
DN 136:185070
ED Entered STN: 26 Feb 2002
TI Epoxy resin-based low-elastic adhesives for semiconductor-loaded substrates
IN Kirihara, Hiroshi; Utono, Michio; Hosokawa, Yoichi
PA Hitachi Chemical Co., Ltd., Japan
SO Jpn. Kokai Tokkyo Koho, 9 pp.
CODEN: JKXXAF
DT Patent
LA Japanese
IC ICM C09J163-00
ICS C08G059-20; C09J133-08; C09J183-04; H01L021-52; H01L023-29; H01L023-31
CC 38-3 (Plastics Fabrication and Uses)
Section cross-reference(s): 39, 76
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2002060716	A	20020226	JP 2000-253234	20000824 <--
PRAI	JP 2000-253234		20000824		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 2002060716	ICM	C09J163-00
	ICS	C08G059-20; C09J133-08; C09J183-04; H01L021-52; H01L023-29; H01L023-31
	IPCI	C09J0163-00 [ICM,7]; C08G0059-20 [ICS,7]; C08G0059-00 [ICS,7,C*]; C09J0133-08 [ICS,7]; C09J0133-06 [ICS,7,C*]; C09J0183-04 [ICS,7]; C09J0183-00 [ICS,7,C*]; H01L0021-52 [ICS,7]; H01L0021-02 [ICS,7,C*]; H01L0023-29 [ICS,7]; H01L0023-31 [ICS,7]; H01L0023-28 [ICS,7,C*]
	IPCR	C08G0059-00 [I,C*]; C08G0059-20 [I,A]; C09J0133-06 [I,C*]; C09J0133-08 [I,A]; C09J0163-00 [I,C*]; C09J0163-00 [I,A]; C09J0183-00 [I,C*]; C09J0183-04 [I,A]; H01L0021-02 [I,C*]; H01L0021-52 [I,A]; H01L0023-28 [I,C*]; H01L0023-29 [I,A]; H01L0023-31 [I,A]

AB The title adhesives, with good temperature-cycle resistance and storage modulus 1000-3000, 20-2000, and 3-50 MPa, at -65°, +25°, and 260°, resp., comprise (a) epoxy resins and hardeners (e.g., EpoTohto YD-8125, EpoTohto YDCN-703, Phenolite LF-2882) 100, (b) epoxy-containing acrylic polymers with glass transition temperature >-10°, weight-average mol. weight >800,000, and glycidyl (meth)acrylate content 2-6% (e.g., HTR-860P3) 50-300, (c) curing accelerators (e.g., Curezol 2PZ-CN) 0.1-10, (d) silicone rubber filler (e.g., Trefil E-601) 20-60, and (e) coupling agents (e.g., NUC A-189, NUC A-1160) 0.1-10 parts.
ST epoxy resin low elastic adhesive semiconductor assembling; acrylic polymer epoxy contg low elastic adhesive; silicone rubber filler low elastic adhesive; coupling agent epoxy resin low elastic adhesive
IT Adhesives
Coupling agents
Semiconductor device fabrication
(epoxy resin-based low-elastic adhesives for semiconductor-loaded substrates)
IT Silicone rubber, uses
RL: MOA (Modifier or additive use); USES (Uses)
(epoxy resin-based low-elastic adhesives for semiconductor-loaded substrates)
IT Epoxy resins, uses
RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)

(epoxy resin-based low-elastic adhesives for semiconductor-loaded substrates)

IT Phenolic resins, uses
RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)
(epoxy, novolak, o-cresol-based; epoxy resin-based low-elastic adhesives for semiconductor-loaded substrates)

IT Acrylic rubber
RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)
(epoxy-containing; epoxy resin-based low-elastic adhesives for semiconductor-loaded substrates)

IT Phenolic resins, uses
RL: MOA (Modifier or additive use); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)
(novolak, bisphenol A-based, hardeners; epoxy resin-based low-elastic adhesives for semiconductor-loaded substrates)

IT Epoxy resins, uses
RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)
(phenolic, novolak, o-cresol-based; epoxy resin-based low-elastic adhesives for semiconductor-loaded substrates)

IT 4420-74-0, NUC A-189 23779-32-0, NUC A-1160
RL: MOA (Modifier or additive use); USES (Uses)
(coupling agents; epoxy resin-based low-elastic adhesives for semiconductor-loaded substrates)

IT 23996-12-5, Curezol 2PZ-CN
RL: CAT (Catalyst use); USES (Uses)
(epoxy resin-based low-elastic adhesives for semiconductor-loaded substrates)

IT 25085-99-8, EpoTohto YD-8125 101706-82-5, EpoTohto YDCN-703
RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)
(epoxy resin-based low-elastic adhesives for semiconductor-loaded substrates)

IT 183748-53-0, Phenolite LF-2882
RL: MOA (Modifier or additive use); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)
(hardeners; epoxy resin-based low-elastic adhesives for semiconductor-loaded substrates)

* NOTICES *

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1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to low elastic adhesives, low elastic jointing material, the substrate for semi-conductor loading, and a semiconductor device.
[0002]
[Description of the Prior Art] In recent years, development of the compact package to which the semiconductor package carried in this with the miniaturization of electronic equipment is called CSP (chip-size package) and muBGA (ball grid array) while the high density assembly to a substrate comes to be required and a miniaturization and lightweight-ization progress is furthered. Although it is reliable as one of the essential properties of a mounting substrate which carried various electronic parts, since especially connection dependability is directly related to the quality of the device which used the mounting substrate, it serves as a very important item.
[0003] The thermal stress produced from the difference of the coefficient of thermal expansion of the substrate which mounts a semiconductor chip and electronic parts as a cause of reducing this connection dependability is mentioned. Since the coefficient of thermal expansion of the patchboard which mounts electronic parts to a thing with the coefficient of thermal expansion of a semiconductor chip small in degree C and about 4 ppm /was large in degree C and 15 ppm /or more, when distortion produced by the thermal shock occurs, thermal stress generates this by the distortion. For example, in bare chip mounting, thermal stress concentrated on the solder ball part which connects the wiring pad of a patchboard with the electrode of a semiconductor chip, and connection dependability was reduced. Although distribution of this thermal stress found that it was effective to pour in the resin called under-filling between a chip and a patchboard, it had become the cause of the increment in a mounting process, and a cost rise.
[0004] Between the wiring substrates which much structure is proposed by CSP, for example, are called a semiconductor chip and INTAPOZA in muBGA as these countermeasures, insulating adhesives are used so that the thermal stress produced from each coefficient-of-thermal-expansion difference can be reduced. The result in which the adhesive film of workability of low elasticity is good, and connection dependability is high as insulating adhesives in recent years is reported (Japanese Patent Application No. No. 266640 [eight to], public presentation WO 98/No. 15975), and others, an adhesive property, temperature cycle nature, moisture resistance, and fire retardancy are demanded as physical properties of a low elastic adhesive film. [reduction / of a chip and a wiring substrate / thermal stress]
[0005] The adhesive film is used with the flexible printed wiring board etc., and many systems which use acrylonitrile-butadiene rubber as a principal component are used. Moreover, the adhesives with which the both ends to which the adhesives which contain acrylic resin, an epoxy resin, the poly isocyanate, and an inorganic filler in JP,60-243180,A have a urethane bond in acrylic resin, an epoxy resin, and a molecule again at JP,61-138680,A as what raised the solder thermal resistance after moisture absorption as a printed wired board related ingredient contain a primary amine compound and an inorganic filler are proposed.

[0006]
[Problem(s) to be Solved by the Invention] The adhesive film which uses acrylonitrile-butadiene rubber as a principal component has the large fall of the adhesive strength at the time of carrying out long duration processing at an elevated temperature, and its degradation at the time of performing a humidity test under severe conditions, such as PCT (pressure cooker test) processing for which it is inferior to electric corrosion-proof nature, and is especially used by the reliability evaluation of a semi-conductor associated part, is large. Although it has such thermal resistance and moisture resistance and the epoxy resin, the curing agent, and the epoxy group content acrylic copolymer are proposed by Japanese Patent Application No. No. 266640 [eight to] as an adhesive film of low elasticity, in a heat cycle test, the trouble that a crack arises is in the pasted-up semiconductor chip.
[0007] A heat cycle test is the test approach of carrying out the pan of the semi-conductor associated part to low temperature (-65 degrees C - -25 degrees C) and an elevated temperature (100-200 degrees C) about 100 to 1000 times by turns, and evaluating dependability. Especially with the conventional adhesives, the modulus of elasticity became high in the low-temperature field, and it had become the cause of making a chip generating a crack. Moreover, after lowering the elastic modulus in low temperature simply, there was a problem to which the dependability in elevated temperatures, such as PCT processing, falls, and coexistence of this property was a big technical problem.
[0008] This invention offers the substrate for semi-conductor loading and a semiconductor device equipped with the low elastic adhesives and the low elastic jointing material which have a low elastic modulus in the low temperature which it has [low temperature] required thermal resistance and moisture resistance when it mounts a semiconductor chip with the large difference of a coefficient of thermal expansion in the wiring substrate called INTAPOZA, such as a glass epoxy group plate and a flexible substrate, and does not make a chip produce a crack in a heat cycle test, and this.
[0009]
[Means for Solving the Problem] This invention relates to the following invention.
(1) Tg (glass transition temperature) in which the sum total of an epoxy resin and its curing agent contains the 100 weight sections and 2 - 6 % of the weight of (2) glycidyl (meta) acrylate -- more than -10 degree C -- and the low elastic adhesives containing the epoxy group content acrylic copolymer [whose weight average molecular weight is 800,000 or more] 50 300 weight sections (3) hardening-accelerator 0.1 - 10 weight sections (4) silicone-rubber filler 20 - 60 weight sections, and the (5) coupling agent 0.1 - 10 weight sections.
(2) Low elastic adhesives of (1) which the storage modulus of the hardened material measured using the dynamic viscoelasticity measuring device is 1000-3000MPa at -65 degrees C, is 20-2000MPa at 25 degrees C, and is 3-50MPa at 260 degrees C.
[0010] (3) (1) or (2) low elastic adhesives whose particle size of a silicone rubber filler is 10 micrometers or less.
(4) (1) or (2) low elastic adhesives which were changed into the condition of having finished 10 - 40% of generation of heat of the full hard-ized calorific value at the time of measuring using DSC (differential scanning calorimetry).
(5) (1) or (2) low elastic adhesives which blended the ion scavenger.
(6) (1) or (2) low elastic adhesives whose rate of 2 organic-functions epoxy resin in an epoxy resin is 70 % of the weight or more.
(7) Low elastic jointing material in which the layer of one low elastic adhesives of (1) - (6) was formed to one side or both sides of a base material.
(8) The substrate for semi-conductor loading which equipped the semiconductor chip loading side of a wiring substrate with the low elastic jointing material of (7).
The semiconductor device using the substrate for semi-conductor loading of (9) and (8).
[0011] This invention relates to the epoxy group content acrylic copolymer which distributed the specific silicone rubber filler with the low elastic modulus in 0 degree C or less, and the adhesives of an epoxy resin system. Since an epoxy group content acrylic copolymer has the low elastic modulus near a room temperature, by enlarging the mixing ratio of an epoxy group content acrylic copolymer, it

originates in the difference of the coefficient of thermal expansion of a semiconductor chip and a wiring substrate, and can control a crack according to the effectiveness which eases the stress generated in the heating cooling process at the time of a reflow.
[0012] Moreover, since an epoxy group content acrylic copolymer is excellent in reactivity with a curing agent like an epoxy resin, and the hardened material of low elastic adhesives is stabilized chemically and physically, it shows the engine performance excellent in the humidity test represented by PCT processing. Moreover, the silicone rubber filler is excellent in distributed stability with an epoxy resin, and it can carry out [low elasticity]-izing at low temperature, without spoiling the property which was excellent as adhesives. Moreover, by this invention, where it dissolved in the organic solvent for varnish production beforehand and an epoxy resin and its curing agent, and a silicone rubber filler are mixed, after DISUPA etc. performs distributed processing, the distributed stability of the silicone rubber filler within a varnish and many physical properties of an adhesive film are secured by blending a coupling agent, an epoxy group content acrylic copolymer, and a hardening accelerator. Moreover, by this invention, where it dissolved in the organic solvent for varnish production beforehand and an epoxy group content acrylic copolymer and a silicone rubber filler are mixed, after DISUPA etc. performs distributed processing, the distributed stability of the silicone rubber filler within a varnish and many physical properties of an adhesive film are secured by blending with an epoxy resin and its curing agent, a coupling agent, and a hardening accelerator.
[0013]
[Embodiment of the Invention] It is two or more organic functions, and let weight average molecular weight more preferably be a with a weight average molecular weight of less than 3000 epoxy resin less than 5000 that the epoxy resin used by this invention should just be what hardens and presents an adhesion operation. As a 2 organic-functions epoxy resin, bisphenol A mold or bisphenol female mold liquefied resin etc. is illustrated. Bisphenol A mold or bisphenol female mold liquefied resin is marketed by the trade name of YD8125 and YDF170 from Tohto Kasei Co., Ltd. As an epoxy resin, a polyfunctional epoxy resin may be added for the purpose of a raise in Tg, and a phenol novolak mold epoxy resin, a cresol novolak mold epoxy resin, etc. are illustrated as a polyfunctional epoxy resin. The phenol novolak mold epoxy resin is marketed by the trade name of EPPN-201 from Nippon Kayaku Co., Ltd. From Sumitomo Chemical Co., Ltd., a cresol novolak mold epoxy resin is the trade name of ESCN-001 and ESCN-195, and is marketed by the trade name of said Nippon Kayaku Co., Ltd. to EOCN1012, EOCN1025, and EOCN1027. It is marketed by the trade name of YDCN-703 from Tohto Kasei Co., Ltd.
[0014] Since an adhesives layer will become weak if there are too many polyfunctional epoxy resins, the compounding ratio of a 2 organic-functions epoxy resin and a polyfunctional epoxy resin is more preferably made into 90 % of the weight or more 70% of the weight or more in the loadings of a 2 organic-functions epoxy resin. What is usually used as a curing agent of an epoxy resin can be used for a curing agent, and bisphenol A, Bisphenol F, Bisphenol S, etc. which are the compound which has an amine, a polyamide, an acid anhydride, a polysulfide, boron trifluoride, and a phenolic hydroxyl group in [two or more] 1 molecule are mentioned. Since it excels in the electric corrosion-proof nature at the time of moisture absorption, it is desirable to use phenol novolak resin, bisphenol novolak resin, or cresol novolak resin.
[0015] Thus, especially the desirable curing agent is marketed from Dainippon Ink & Chemicals, Inc. by the trade name of the FENO light LF 2882, the FENO light LF 2822, FENO light TD-2090, FENO light TD-2149, the FENO light VH4150, and the FENO light VH4170. An epoxy resin can secure an adhesive property with 25 - 75 weight section and a curing agent as expensive at a rate of 75 - 25 weight section as the wettability of adhesives from the manifestation of an adhesive property [sum total / of an epoxy resin and a curing agent] to a total of 100 weight sections. It is desirable for a hardening accelerator to be used with a curing agent and to use various imidazole derivatives as a hardening accelerator. As an imidazole, 2-methylimidazole, 2-ethyl-4-methylimidazole, 1-cyanoethyl-2-phenylimidazole, 1-cyano ethyl-2-phenyl imidazolium trimellitate, etc. are mentioned.
[0016] Imidazole derivatives are marketed from Shikoku Chemicals Corp. by the trade name of 2E4MZ,

2 PZ-CN, and 2 PZ-CNS. As for a hardening accelerator, it is desirable to add in the range of 0.1 - 10 weight section to a total of 100 weight sections of an epoxy resin and its curing agent from a viewpoint which hardening of adhesives is not advanced beyond the need and secures long term stability. As an epoxy group content acrylic copolymer whose Tg (glass transition temperature) containing 2 - 6 % of the weight of glycidyl (meta) acrylate is more than -10 degree C and whose weight average molecular weight is 800,000 or more, trade name HTR-860P-3 marketed, for example from imperial chemistry industrial incorporated company can be used. The amount of the glycidyl (meta) acrylate used as a functional-group monomer is made into 2 - 6 % of the weight. In order to obtain adhesive strength, it considers as 2 % of the weight or more, and in order to prevent gelation of rubber, it may be 6 or less % of the weight. Although the remainder can use the mixture of ethyl (meta) acrylate, butyl (meta) acrylate, or both, a mixed ratio is determined in consideration of Tg of a copolymer. Since the tuck nature of the adhesive film in B stage condition becomes it large that Tg is less than [-10 degree C] and handling nature gets worse, it may be -10 degrees C or more. It can obtain according to pearl polymerization, solution polymerization, etc.

[0017] Although weight average molecular weight of an epoxy group content acrylic copolymer is made or more into 800,000, in this range, it is because there are little reinforcement in the shape of the shape of a sheet and a film, flexible fall, and increase of tuck nature. If it is carried out to more than 50 weight sections, and there are many phases of a rubber component and an epoxy resin phase decreases, in order to prevent that a fall and tuck nature of the reinforcement of a film become large, since the fall of the handling nature in an elevated temperature will take place, the addition of an epoxy group content acrylic copolymer is made below into the 300 weight sections. The trade name TOREFIRU E series by which the silicone rubber filler is marketed from the trade name X-52-830 marketed from Shin-Etsu Chemical Co., Ltd., X-52-854, and Dow Corning Toray Silicone, Inc. is used. Let the amount of the silicone rubber filler used be 20 - 60 weight section from reservation of film reinforcement, and the field of an elastic modulus to an epoxy resin and its curing agent 100 weight section.

[0018] As a coupling agent, a silane coupling agent is desirable. As a silane coupling agent, gamma-glycidoxypropyltrimetoxysilane, gamma-mercapto propyltrimethoxysilane, gamma-aminopropyl triethoxysilane, gamma-ureido propyl triethoxysilane, N-beta-aminoethyl-gamma-aminopropyl trimethoxysilane, etc. are mentioned. For the above mentioned silane coupling agent, gamma-glycidoxypropyltrimetoxysilane is NCU. A-187 and gamma-mercapto propyltrimethoxysilane are NCU. A-189 and gamma-aminopropyl triethoxysilane are NCU. A-1100 and gamma-ureido propyl triethoxysilane are NCU. A-1160 and N-beta-aminoethyl-gamma-aminopropyl trimethoxysilane are NCU. It is the trade name of A-1120, and each is marketed from Nippon Unicar, Inc., and it can be used suitably. Let the loadings of a coupling agent be 0.1 - 10 weight section from the effectiveness by addition, or thermal resistance and cost to an epoxy resin and its curing agent 100 weight section.

[0019] Furthermore, an ion scavenger can be blended, in order to adsorb an ionicity impurity and to improve the insulating dependability at the time of moisture absorption. The loadings of an ion scavenger have 5 - 10 weight section more desirable than effectiveness, and the thermal resistance and cost by addition to an epoxy resin and its curing agent 100 weight section. Since it prevents copper ionizing and beginning to melt as an ion scavenger, the compound known as copper inhibitor, for example, triazine thiol compounds, a bisphenol system reducing agent, etc. can also be blended. As a bisphenol system reducing agent, 2,2'-methylene bis - (the [4-methyl-6-] 3-butylphenol), 4,4'-thiobis - (the [3-methyl-6-] 3-butylphenol), etc. are mentioned.

[0020] The copper inhibitor which uses triazine thiol compounds as a component is marketed by the trade name of JISUNETTO DB from Sankyoseiyakukogyo Corp. Moreover, the copper inhibitor which uses a bisphenol system reducing agent as a component is marketed by the trade name of reed NOx BB from Yoshitomi Pharmaceutical Industries, Ltd. As for the solvent of varnish-izing, it is desirable to use the methyl ethyl ketone of a low-boiling point, an acetone, methyl isobutyl ketone, 2-ethoxyethanol, toluene, butyl cellosolve, a methanol, ethanol, 2-methoxyethanol, etc. comparatively. Moreover, a high boiler may be added for the purpose of improving paint film nature. Dimethylacetamide, dimethylformamide, a methyl pyrrolidone, a cyclohexanone, etc. are mentioned as a high boiler.

[0021] Moreover, if the particle size of a silicone rubber filler is 10 micrometers or less, since the condition that distribution within a varnish was stabilized can be kept long in this invention, it is desirable. As a particle size of a silicone rubber filler, it is still still more desirable that it is 5 micrometers or less from a viewpoint of the long term stability of a varnish. A stone milling machine, 3 rolls, DISUPA, etc. can perform distributed adjustment of a silicone rubber filler again combining these. Moreover, after considering as a varnish, it is desirable to remove the air bubbles in a varnish by the vacuum deairing. In this way, in case the produced varnish is applied to a thin film on a base material and an adhesives layer is produced, the distributed stability of each component blended into a varnish is high, and high bond strength can be secured, without producing the extremely thin part of the film thickness called crawling at the time of coating.
[0022] The above-mentioned adhesives varnish can be applied on base materials, such as a heat-resistant film, and can carry out stoving, a solvent can be removed, and an adhesive film can be obtained. As the quality of the material, polyethylene terephthalate (henceforth, PET), a polyamide, polyimide, a polyether ether ketone, polystyrene, etc. are mentioned. Moreover, it is desirable for a base material to also have the application which is removed and is used as a monolayer article of an adhesives layer, and to carry out mold release processing with silicone etc. on the surface of a base material in that case. Although especially the coating approach is not limited, a roll coat, a reverse roll coat, a gravure coat, a lip coat, a bar coat, etc. are mentioned, for example.
[0023] Moreover, the low elastic jointing material which has a low elastic adhesives layer to one side or both sides of a base material is obtained by applying and heating low elastic adhesives to one side or both sides of a base material, and removing a solvent. Moreover, the low elastic adhesives layer applied on the base material may be stuck on both sides of a base material by the lamination. As for the pressure of a lamination, at this time, it is desirable to carry out by the pressure to which deformation of an adhesive film does not take place. When forming a low elastic adhesives layer in both sides, the thickness of the adhesives layer of one side and other sides may differ.
[0024] measurement of Tg (glass transition temperature) of the epoxy group content acrylic copolymer in this invention -- Mac the hardening film cut in distance between chucks of 15mm at width of face of 4mm using the 4000 mold TMA made from Science -- attaching -- 5g of tension loads, and temperature requirements [a part for /and 30-250 degrees C of programming-rate measurement temperature requirements of 10 degrees C] conditions -- heat -- a variation rate -- an amount is measured. As for the low elastic adhesives which become this invention, it is desirable to consider as the condition of having finished 10 - 40% of generation of heat of the full hard-ized calorific value measured using DSC (differential scanning calorimetry). Although it heats in case a solvent is removed, the hardening reaction of the constituent of low elastic adhesives progresses and gels at this time. The hardening condition in that case influences the fluidity of adhesives, and fitness-izes an adhesive property and handling nature. In the measurement temperature requirement, the null-balance method which supplies or removes a heating value is made into a measurement principle so that a temperature gradient with a standard sample without generation of heat and endoergic may be negated continuously, the measuring device is marketed, and DSC can be measured using it.
[0025] The reaction of the resin constituent of low elastic adhesives is exothermic reaction, if the sample is heated with the fixed programming rate, a sample will react and a heating value will generate it. The calorific value is outputted to a chart, and it asks for the area surrounded by the exoergic curve and the base line on the basis of the base line, and let this be calorific value. It measures with 10-degree-C programming rate for /from a room temperature to 250 degrees C, and the above-mentioned calorific value is calculated. Next, the calorific value of the low elastic adhesives which applied to the above-mentioned base material, and were dried and obtained is calculated as follows. First, the total heating value of a non-hardened sample which dried the solvent using the vacuum dryer at 25 degrees C is measured, and this is set to A (J/g). Next, the calorific value B of coating and the dry sample is measured, and C (%) and the (condition of having finished generation of heat by heating and desiccation) are given by the following formula whenever [hardening / of a sample].
C (%) =(A-B)x100/A [0026] As for the storage modulus which measured the hardened material of the

low elastic adhesives of this invention with the dynamic viscoelasticity measuring device, it is desirable for it to be made as 20-2000MPa at 1000-3000MPa and 25 degrees C, and to make it into the low elastic modulus of 3-50MPa at 260 degrees C by -65 degrees C. It is performed in the temperature dependence measurement mode measured from -100 degrees C to 200 degrees C by part for frequency [of 10Hz], and programming-rate/of 5-10 degrees C, pulling measurement of a storage modulus to the hardened material of fire-resistant adhesives, and applying a load. - In that by which the storage modulus in 65 degrees C exceeds 3000MPa(s), since the effectiveness of making the stress generated according to the difference of the thermal expansion of a semiconductor chip and a wiring substrate at the time of a heat cycle test easing becomes small, it is easy to generate a crack. On the other hand, in less than 1000 MPas, since a storage modulus [in / in a storage modulus / 25 degrees C] becomes less than 20, it is not desirable. In that by which the storage modulus in 25 degrees C exceeds 2000MPa(s), since the effectiveness of making the stress generated according to the difference of the thermal expansion of a semiconductor chip and a wiring substrate at the time of a reflow easing becomes small, it is easy to generate a crack. On the other hand, a storage modulus is inferior to the handling nature of adhesives by less than 20 MPas. Moreover, it is not desirable in order that the storage modulus in 25 degrees C may exceed 2000MPa(s), when it is inferior to the thermal resistance in solder temperature in less than 3 MPas at 260 degrees C and exceeds 50MPa.

[0027] The substrate used for the substrate for semi-conductor loading of this invention can be used without being caught by the substrate quality of the materials, such as a ceramic and an organic substrate. As a configuration of wiring, one side, both sides, and which structure of a multilayer interconnection are sufficient, and the through tube and the non-through tube which were connected electrically if needed may be prepared. When wiring furthermore appears in the outer surface of a semiconductor device, it is desirable to prepare a protection resin layer. Moreover, although the approach of carrying out thermocompression bonding of the jointing material cut in the predetermined configuration according to a package configuration about the pasting approach to the substrate of jointing material to the request location on a wiring substrate or the approach of laminating jointing material on a circuit board with a long picture is common, it is not limited to this.

[0028] Drawing 1 is the sectional view of the low elastic jointing material formed in the combination of the low elastic adhesives layer 1 of this invention, and a base material 2, and shows the low elastic jointing material which forms the low elastic adhesives layers 1 and 1 in both sides of the base material 2 as shown in the monolayer article and drawing 1 (b) of the low elastic adhesives 1 as shown in drawing 1 (a), and is obtained. Drawing 2 shows the sectional view of the semiconductor device in which one example of this invention is shown (muBGA structural drawing). Drawing 2 (a) is the sectional view of a semiconductor device in which the semiconductor chip 5 was pasted up on the substrate 4 for semi-conductor loading which equipped the semiconductor chip loading side of a wiring substrate with the low elastic jointing material which consists of a monolayer of the low elastic adhesives 1 of this invention, some wiring 3 was connected to the bonding pad of a semiconductor chip as a semiconductor chip connection member 6, the perimeter of a semiconductor chip was closed with the sealing agent 7, and the external connection terminal 8 was formed. Drawing 2 (b) is the sectional view of the semiconductor device using the low elastic jointing material which forms the low elastic adhesives layer 1 in both sides of the base material 2 of the low elastic jointing material of (a), and is obtained. The semiconductor device on which the semiconductor chip and the substrate for semi-conductor loading were pasted up using the low elastic jointing material of this invention is excellent in reflow-proof nature, a heat cycle test, moisture resistance (PCT-proof nature), etc. Hereafter, an example explains this invention still more concretely.

[0029]

[Example] As an epoxy resin, the bisphenol A mold epoxy resin (weight-per-epoxy-equivalent 175 and YD-8125 by Tohto Kasei Co., Ltd. are used) 70 weight section, (Constituent varnish 1 of adhesives) As a curing agent, the bisphenol A novolak resin (Dainippon Ink 2882 [LF-] are used) 30 weight section, After carrying out mixed churning of the silicone rubber filler (TOREFIRU E-601 by Dow Corning, Toray Industries, is used) 40 weight section and carrying out distribution by DISUPA on the varnish

which carried out churning mixing of the cyclohexanone 30 weight section as a solvent, as an epoxy group content acrylic copolymer -- epoxy group content acrylic rubber (molecular weight 1 million --) HTR-860P-3 by imperial chemistry industrial incorporated company The use 230 weight section, As a hardening accelerator, the 1-cyanoethyl-2-phenylimidazole (cure ZORU 2 PZ-CN is used) 0.5 weight section, As a coupling agent Gamma-glycidoxypropyltrimetoxysilane For the low elastic adhesives component which consists of the 2.5 weight sections and the gamma-ureido propyl triethoxysilane (NUCA-1160 by Nippon Unicar, Inc. are used) 2.5 weight section, (NUC A-189 by Nippon Unicar, Inc. are used) As a solvent The 1700 weight sections were added, churning mixing of the cyclohexanone was carried out, and the constituent varnish 1 of these adhesives was obtained. The particle size of the silicone rubber filler after DISUPA processing was 5-10 micrometers. As a result of measuring the storage modulus of the hardened material of these low elastic adhesives using a dynamic viscoelasticity measuring device, they were 4MPa(s) at 450MPa(s) and 260 degrees C in 2600MPa(s) and 25 degrees C by -65 degrees C.

[0030] (Constituent varnish 2 of adhesives) By the same combination as the constituent 1 of adhesives, after mixing a silicone rubber filler for an acrylic rubber component, DISUPA processing was performed, mixed churning below of an epoxy component was carried out after that, and the constituent varnish 2 of these adhesives was obtained. The particle size of the silicone rubber filler after DISUPA processing was 10-20 micrometers. As a result of measuring the storage modulus of the hardened material of these low elastic adhesives using a dynamic viscoelasticity measuring device, they were 4MPa(s) at 500MPa(s) and 260 degrees C in 2700MPa(s) and 25 degrees C by -65 degrees C.

[0031] As an epoxy resin, the bisphenol A mold epoxy resin (weight-per-epoxy-equivalent 175 and YD-8125 by Tohto Kasei Co., Ltd. are used) 60 weight section, (Constituent varnish 3 of adhesives) The epoxy resin (YDCN-703 by Tohto Kasei Co., Ltd. are used) 5 weight section of a phenol novolak mold, As a curing agent, the bisphenol A novolak resin (Dainippon Ink 2882 [LF-] are used) 35 weight section, After carrying out silicone rubber filler (TOREFIRU E-601 by Dow Corning, Toray Industries, is used) 40 weight section mixing churning and carrying out distribution by DISUPA on the varnish which carried out churning mixing of the cyclohexanone 30 weight section as a solvent, as an epoxy group content acrylic copolymer -- epoxy group content acrylic rubber (molecular weight 1 million --) As the HTR-860P-3 230 weight section by imperial chemistry industrial incorporated company, and a hardening accelerator, the 1-cyanoethyl-2-phenylimidazole (cure ZORU 2 PZ-CN is used) 0.5 weight section, As a coupling agent Gamma-glycidoxypropyltrimetoxysilane For the low elastic adhesives component which consists of the 2.5 weight sections and the gamma-ureido propyl triethoxysilane (NUC A-1160 by Nippon Unicar, Inc. are used) 2.5 weight section, (NUC A-189 by Nippon Unicar, Inc. are used) As a solvent a cyclohexanone -- the 1700 weight sections -- in addition, churning mixing was carried out and the constituent varnish 1 of these adhesives was obtained. The particle size of the silicone rubber filler after DISUPA processing was 5-10 micrometers. As a result of measuring the storage modulus of the hardened material of these low elastic adhesives using a dynamic viscoelasticity measuring device, they were 7MPa(s) at 500MPa(s) and 260 degrees C in 2800MPa(s) and 25 degrees C by -65 degrees C.

[0032] (Example 1 of a comparison)

As an epoxy resin, the bisphenol A mold epoxy resin (weight-per-epoxy-equivalent 175 and YD-8125 by Tohto Kasei Co., Ltd. are used) 70 weight section, (Constituent varnish 4 of adhesives) As a curing agent, the bisphenol A novolak resin (Dainippon Ink 2882 [LF-]) 30 weight section, the varnish which carried out churning mixing of the cyclohexanone 30 weight section as a solvent -- as an epoxy group content acrylic copolymer -- epoxy group content acrylic rubber (molecular weight 1 million --) HTR-860P-3 by imperial chemistry industrial incorporated company The use 230 weight section, As a hardening accelerator, the 1-cyanoethyl-2-phenylimidazole (cure ZORU 2 PZ-CN is used) 0.5 weight section, As a coupling agent Gamma-glycidoxypropyltrimetoxysilane For the low elastic adhesives component which consists of the 2.5 weight sections and the gamma-ureido propyl triethoxysilane (NUC A-1160 by Nippon Unicar, Inc. are used) 2.5 weight section, (NUC A-189 by Nippon Unicar, Inc. are used) As a solvent The cyclohexanone 1700 weight section was added, churning mixing was carried

out, and the constituent varnish 4 of these adhesives was obtained. As a result of measuring the storage modulus of the hardened material of these adhesives using a dynamic viscoelasticity measuring device, they were 6MPa(s) at 820MPa(s) and 260 degrees C in 3470MPa(s) and 25 degrees C by -65 degrees C.
[0033] (Example 2 of a comparison)
As an epoxy resin, the bisphenol A mold epoxy resin (weight-per-epoxy-equivalent 175 and YD-8125 by Tohto Kasei Co., Ltd. are used) 70 weight section, (Constituent varnish 5 of adhesives) As a curing agent, the bisphenol A novolak resin (Dainippon Ink 2882 [LF-] are used) 30 weight section, On the varnish which carried out churning mixing as a solvent, as a filler the cyclohexanone 30 weight section The antimony-trioxide (NIHON SEIKO PATOX-U is used) 40 weight section, As a coupling agent, the gamma-glycidoxypropyltrimetoxysilane (NUC A-189 by Nippon Unicar, Inc. are used) 2.5 weight section, After carrying out mixed churning of the gamma-ureido propyl triethoxysilane (NUC A-1160 by Nippon Unicar, Inc. are used) 2.5 weight section, bead mill processing -- carrying out -- as an epoxy group content acrylic copolymer -- epoxy group content acrylic rubber (molecular weight 1 million --) HTR-860P-3 by imperial chemistry industrial incorporated company The use 230 weight section, The cyclohexanone 1700 weight section was added to the adhesives component which consists of the 1-cyanoethyl-2-phenylimidazole (cure ZORU 2 PZ-CN is used) 0.5 weight section as a hardening accelerator as a solvent, churning mixing was carried out, and the constituent varnish 5 of these adhesives was obtained. The particle size of the antimonic acid ghost after bead mill processing was 1-5 micrometers. As a result of measuring the storage modulus of the hardened material of these adhesives using a dynamic viscoelasticity measuring device, they were 4.5MPa(s) at 1100MPa(s) and 260 degrees C in 3400MPa(s) and 25 degrees C by -65 degrees C.
[0034] (Example 1) The constituent varnish 1 of adhesives was applied as a carrier film on the **-form-processed polyethylene terephthalate film (Teijin PUREX A-63) with a thickness of 50 micrometers, was dried for 5 minutes at 155 degrees C, the paint film in B stage condition that thickness is 50 micrometers was formed, and the low elastic jointing material equipped with the base material was produced. In addition, whenever [hardening / of the low elastic adhesives in this condition] was in the condition which finished generation of heat of 14 - 20% of within the limits of full hard-ized calorific value, as a result of measuring using DSC (Du Pont 912 mold DSC) (programming rate: a part for 10-degree-C/). Moreover, the amount of residual solvents was 0.1 - 0.5% of the weight of within the limits.
[0035] (Example 2) The low elastic jointing material equipped with the base material was produced like the example 1 except having used the constituent varnish 1 of adhesives as the constituent varnish 2 of adhesives. In addition, whenever [hardening / of the low elastic adhesives in this condition] was in the condition which finished generation of heat of 16 - 20% of within the limits of full hard-ized calorific value, as a result of measuring any adhesives using DSC (Du Pont 912 mold DSC) (programming rate: a part for 10-degree-C/). Moreover, the amount of residual solvents was 0.1 - 0.5% of the weight of within the limits.
[0036] (Example 3) The low elastic jointing material equipped with the base material was produced like the example 1 except having used the constituent varnish 1 of adhesives as the constituent varnish 3 of adhesives. In addition, whenever [hardening / of the low elastic adhesives in this condition] was in the condition which finished generation of heat of 15 - 20% of within the limits of full hard-ized calorific value, as a result of measuring any adhesives using DSC (Du Pont 912 mold DSC) (programming rate: a part for 10-degree-C/). Moreover, the amount of residual solvents was 0.1 - 0.5% of the weight of within the limits.
[0037] (Example 1 of a comparison) The low elastic jointing material equipped with the base material was produced like the example 1 except having used the constituent varnish 1 of adhesives as the constituent varnish 4 of adhesives. In addition, whenever [hardening / of the low elastic adhesives in this condition] was in the condition which finished generation of heat of 15 - 20% of within the limits of full hard-ized calorific value, as a result of measuring any adhesives using DSC (Du Pont 912 mold DSC) (programming rate: a part for 10-degree-C/). Moreover, the amount of residual solvents was 0.7 - 1.5% of the weight of within the limits.
[0038] (Example 2 of a comparison) The jointing material equipped with the base material was

produced like the example 1 except having used the constituent varnish 1 of adhesives as the constituent varnish 5 of adhesives. In addition, whenever [hardening / of the adhesives in this condition] was in the condition which finished generation of heat of 15 - 20% of within the limits of full hard-ized calorific value, as a result of measuring any adhesives using DSC (Du Pont 912 mold DSC) (programming rate: a part for 10-degree-C/). Moreover, the amount of residual solvents was 1.0 - 1.5% of the weight of within the limits. The flow nature at the time of coating, bond strength, and a TCT crack were evaluated using the obtained jointing material. Flow nature is the thermocompression bonding machine of circuit tester industrial incorporated company production about the sample for evaluation which stuck the adhesives layer for the adhesives cut down in fixed size on the slide glass. When carrying out thermocompression bonding on the die temperature of 160 degrees C (both sides), pressure 2MPa, and the conditions for sticking-by-pressure time amount 18 seconds, Flow nature of the adhesives which measured how many adhesives flowed out of the conventional size, and carried out coating immediately after varnish production was set to 100, and what is being changed more than O and it in what will have the flow nature on the 7th within the limits of 80-120 for the 3rd day was made into x.

[0039] Bond strength sandwiches adhesives using the same sticking-by-pressure machine between a glass plate and polyimide (YUPI REXX 50 by Ube Industries, Ltd. S). After carrying out thermocompression bonding on the die temperature of 160 degrees C (both sides), pressure 2MPa, and the conditions for sticking-by-pressure time amount 18 seconds, Leave it for 1 hour, terminate a hardening reaction, and a Peel on-the-strength measurement machine is used for the bottom of a 170-degree C condition 90 degrees by circuit tester industrial incorporated company. The polyimide film tore off, reinforcement was measured and that to which the average of three samples from which it differs at the time of adhesives production exceeds [a less than 200g //cm / thing] ** and 500 g/cm for the thing of x and 200 - 500 g/cm within the limits was made into O. The heat cycle test evaluated by producing the semiconductor device sample which stuck with adhesives the wiring substrate which used a semiconductor chip and a 75-micrometer polyimide film as shown in drawing 2 (a) or (b) for the wiring substrate base material. The process which leaves a sample for 30 minutes in -65-degree-C ambient atmosphere, and is left in a 150-degree C ambient atmosphere after that for 30 minutes was measured as 1 cycle, and except [its] was made into x for what destruction did not produce by 500 cycle by O. The result was shown in Table 1.

[0040]

[Table 1]

項　目	実施例1	実施例2	実施例3	比較例1	比較例2
流れ性	O	O	O	O	O
接着性	O	O	O	O	O
温度サイクル	O	O	O	×	×

[0041] In the examples 1 and 2 of a comparison, the problem to which a crack occurs in a chip by the heat cycle test is produced. By blending a silicone rubber filler, the example 1 was able to obtain the low elastic modulus in -65 degrees C. Moreover, in the example 2, sufficient distributed condition was acquired also by the approach of distributing a silicone rubber filler beforehand to acrylic rubber. In the example 3, 2 organic-functions epoxy resin and the polyfunctional epoxy resin are mixed and used, and high bond strength is obtained with varnish stability.

[0042]

[Effect of the Invention] Since the low elastic adhesives of this invention and low elastic jointing material have the low modulus of elasticity near -65 degree C, they can make the thermal stress generated from the coefficient-of-thermal-expansion difference of a semiconductor chip and a wiring substrate at the time of heating cooling ease in a semiconductor device. Therefore, the crack initiation in a heat cycle test is not accepted, but it excels in stress relaxation nature.

CLAIMS

[Claim(s)]
[Claim 1] (1) Tg (glass transition temperature) in which the sum total of an epoxy resin and its curing agent contains the 100 weight sections and 2 - 6 % of the weight of (2) glycidyl (meta) acrylate -- more than -10 degree C -- and the low elastic adhesives containing the epoxy group content acrylic copolymer [whose weight average molecular weight is 800,000 or more] 50 300 weight sections (3) hardening-accelerator 0.1 - 10 weight sections (4) silicone-rubber filler 20 - 60 weight sections, and the (5) coupling agent 0.1 - 10 weight sections.
[Claim 2] Low elastic adhesives according to claim 1 which the storage modulus of the hardened material measured using the dynamic viscoelasticity measuring device is 1000-3000MPa at -65 degrees C, are 20-2000MPa at 25 degrees C, and are 3-50MPa at 260 degrees C.
[Claim 3] Low elastic adhesives according to claim 1 or 2 whose particle size of a silicone rubber filler is 10 micrometers or less.
[Claim 4] Low elastic adhesives according to claim 1 or 2 changed into the condition of having finished 10 - 40% of generation of heat of the full hard-ized calorific value at the time of measuring using DSC (differential scanning calorimetry).
[Claim 5] Low elastic adhesives according to claim 1 or 2 which blended the ion scavenger.
[Claim 6] Low elastic adhesives according to claim 1 or 2 whose rate of 2 organic-functions epoxy resin in an epoxy resin is 70 % of the weight or more.
[Claim 7] Low elastic jointing material in which the layer of low elastic adhesives according to claim 1 to 6 was formed to one side or both sides of a base material.
[Claim 8] The substrate for semi-conductor loading which equipped the semiconductor chip loading side of a wiring substrate with low elastic jointing material according to claim 7.
[Claim 9] The semiconductor device using the substrate for semi-conductor loading according to claim 8.

[Translation done.]